Dissolution Kinetics of UO_2 (cr)

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Background

The dissolution rate of crystalline uranium (IV) dioxide under environmental conditions has been studied for four decades ([1], [2], and [3]). Several inconsistencies arise when normalizing and comparing existing data. We surmise that these inconsistencies exist because the forward rate of reaction was not achieved during many of these experiments. In an attempt to solve these inconsistencies a series of flow-through experiments at pH=8.5, [HCO_3^-]=0.1 M, and T=30º and 60ºC (Figure 1) were conducted.

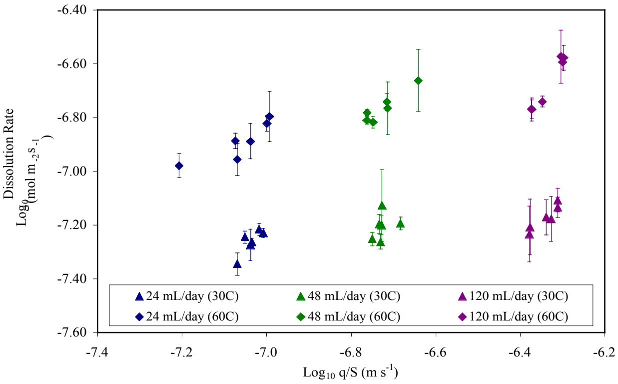

Figure 1: Log_{10} Rate vs. Log_{10} (q/S) at T = 30ºC and 60ºC

Discussion of results

A plot of rate versus ratio of flow rate, q, to sample surface area, S, indicates that the elemental release rate of uranium is not only dependant on temperature but also flow rate and surface area. These results can be interpreted as evidence for dissolution at the forward rate of reaction, although more data are needed.

Conclusions

The rates obtained in this study are 1 to 2 orders of magnitude faster than previously reported rates and may reflect the dependence of rates on the ratio of q/S. These results highlight the importance of understanding the role between solution saturation state and dissolution kinetics.

References

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Isotopic variations in the sediments of the Caspian Sea: a record for the quaternary continental weathering?

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Geochemical and isotopic variations in the sediment of the Caspian Sea have been addressed to identify 1) the processes having induced these variations and 2) the possible influence of the main climatic changes in the region during the Quaternary.

We have combined mineralogical, chemical, and isotopic (Sr isotopic ratios and U/Th radioactive disequilibria) analyses on whole sediments and on different mineral phases (carbonates and clays) from a 10-m long core with Late Pleistocene and Holocene records and located in the Southern part of the Caspian Sea at 518 m depth.

The chemical and mineralogical results allowed us to divide the sedimentary sequence into two main units. The lower (U1) consists mainly in silicic minerals, whereas the upper (U2) is characterised by carbonates. The transition between U1 and U2 correspond to the end of the last deglaciation.

The chemical and Sr isotopic compositions of the whole sediments and of the clays varied between U1 and U2 which imply change in the origin of the detrital fraction. The results seem to illustrate a modification of the sources of materials carried by rivers to the Caspian Sea, and thus a change in the drainage area.

The $^{234}U/^{238}U$ and the $^{230}Th/^{234}U$ ratios obtained on the whole sediment, as well as on the carbonates and clays of U1 are relatively constant and close to the secular equilibrium. These results cannot result from an aging effect and certainly represent a predominant mechanical alteration of old material in the drainage area of the Caspian Sea during deposition of U1.

To the opposite, the $^{230}Th/^{234}U$ ratios become lower than 1 in the upper units U2 and the$^{234}U/^{238}U$ ratios increase towards the present-day Caspian sea water which implies an evolution of the weathering with a progressive U-Th fractionation.

These results suggests an evolution of the weathering conditions in the drainage basin of the Caspian Sea from mechanical erosion during cold period to a more chemical weathering since almost 10,000 yr (corresponding to the U1/U2 transition).